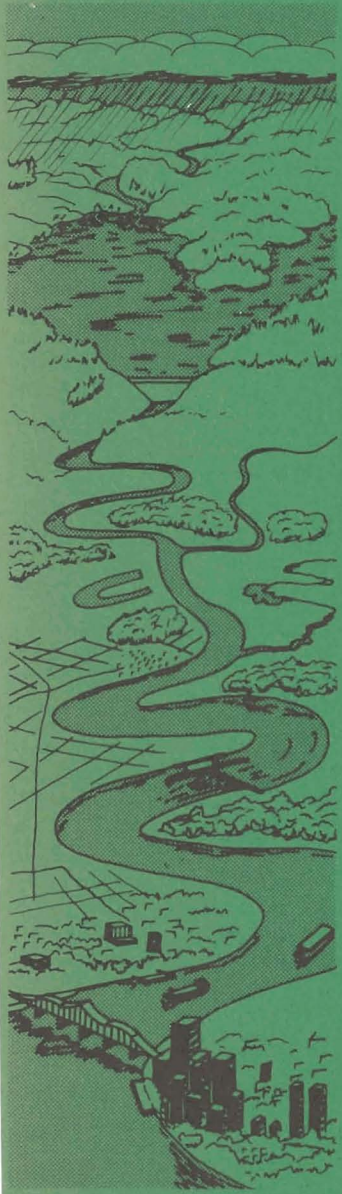




US Army Corps
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ANAEROBIC AND AEROBIC RATE COEFFICIENTS FOR USE IN CE-QUAL-R1

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Anaerobic and aerobic rate coefficients for iron, manganese, orthophosphate-P, ammonium-N, and other nutrients were determined for a wide variety of reservoir sediments using laboratory reactor units. Predicted anaerobic rate coefficients derived using diffusion equations were compared to observed anaerobic rate coefficients for iron, manganese, ammonium-N, and orthophosphate-P. Actual ammonium-N release rates closely paralleled release (Continued)		

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rates predicted by diffusion equations; release rates for iron, manganese, and orthophosphate-P consistently exceeded predicted release rates. Remobilization of iron, manganese, and orthophosphate from the aerobic surface sediment layer during anaerobic conditions was postulated as the cause of the enhanced releases observed.

Aerobic rate coefficients obtained in field and laboratory studies for total inorganic nitrogen, NH_4^+ -N, and iron were not statistically different. Manganese oxidation rates, NO_3^- -N accumulation, and orthophosphate-P disappearance measured in the field were not comparable to laboratory derived rates, presumably due to dilution and other complex environmental effects.

The rate data presented in this report are for use in CE-QUAL-R1 and other water quality models. Recommended procedures for selection of appropriate anaerobic and aerobic rate coefficients are discussed.

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PREFACE

This study was sponsored by the Office, Chief of Engineers (OCE), U. S. Army, as a part of the Environmental Water Quality and Operational Studies (EWQOS), Work Unit 31594 (IB.2), entitled "Develop and Verify Descriptions for Reservoir Chemical Processes." The OCE Technical Monitors for EWQOS were Mr. Earl E. Eiker, Dr. John Bushman, and Mr. James L. Gottesman.

The work was conducted during the period September 1978-September 1983 by the Environmental Laboratory, U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, under the direction of Dr. John Harrison, Chief of the Environmental Laboratory (EL), and under the general supervision of Mr. D. L. Robey, Chief of the Ecosystem Research and Simulation Division (ERSD), and Dr. T. L. Hart, Chief of the Aquatic Processes and Effects Group. Program Manager of EWQOS was Dr. J. L. Mahloch, EL. Some of the foundation work for this study was performed as part of the Corps of Engineers In-House Laboratory Independent Research Program (ILIR), Work Unit 111 06, entitled "Mechanisms that Regulate the Degree of Oxidation-Reduction in Anaerobic Sediments and Natural Water Systems."

This study was conducted by Drs. R. L. Chen, J. M. Brannon, and D. Gunnison, ERSD. Mr. I. Smith, Jr., and Mr. T. Sturgis, ERSD, assisted with the laboratory experimentation. This report was written by Drs. Chen, Brannon, and Gunnison and was reviewed by Dr. R. M. Engler and Mr. J. B. Waide.

Directors of WES during the study and preparation of this report were COL Nelson P. Conover, CE, and COL Tilford C. Creel, CE. Technical Director was Mr. F. R. Brown.

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ANAEROBIC AND AEROBIC RATE COEFFICIENTS FOR USE IN CE-QUAL-R1

PART I: INTRODUCTION

Background

1. Many Corps of Engineers (CE) reservoirs exhibit low concentrations of dissolved oxygen and high concentrations of products of anaerobic transformation within the hypolimnion, and in some projects, within the metalimnion. Subsequently, anaerobic products may be released with waters withdrawn from these reservoir zones. The adverse impacts of low dissolved oxygen in reservoirs and their releases have included harmful effects on aquatic biota, such as fish kills; high operation and maintenance costs, especially as a result of corrosion; and increased costs to downstream water users due to increased requirements for water treatment.

2. Natural or mechanical introduction of oxygen into an anoxic hypolimnion or metalimnion or anaerobic release waters will rapidly alleviate many water quality problems caused by reduced chemical substances. Improvement in water quality during the change from anaerobic to aerobic conditions is a consequence of the oxidation of metals and nutrients, resulting in speciation and solubility changes that benefit water quality.

3. Gunnison and Brannon (1981) described changes in reservoir water quality created by low dissolved oxygen and anaerobic conditions and formulated a conceptual model to describe these processes. Chen, Gunnison, and Brannon (1983) described changes in anaerobic waters occurring during aeration and presented a conceptual model of these aeration processes. These anaerobic and aerobic processes are being incorporated into CE-QUAL-R1, a mathematical model of water quality.

4. CE-QUAL-R1 describes the vertical distribution of thermal energy and biological and chemical materials in a reservoir through time. It is used to study preimpoundment and postimpoundment water quality problems and the effects of reservoir management operations on water quality. In addition, the model addresses problems of water

quality associated with reservoir eutrophication and anaerobic conditions.

5. CE-QUAL-R1 currently simulates the dynamics of 34 water quality factors, calculating both vertical in-pool and downstream release magnitudes. The model requires an extensive database including initial conditions, geometric and physical coefficients, biological and chemical reaction rates, and time sequences of hydrometeorological and inflowing water quality quantities. At the present time, appropriate anaerobic and aerobic rate coefficients and guidance for their selection do not exist. These coefficients must be developed before modeling approaches can adequately predict the impacts of anaerobic conditions and subsequent reaeration in reservoirs.

Purpose

6. The objectives of this study are (a) to provide anaerobic and aerobic rate coefficients for both aerobic and anaerobic processes, as obtained in laboratory and field studies; (b) to provide guidance for selection of appropriate rate coefficients; and (c) to provide procedures for interpretation and evaluation of relevant rate data. Data in this report are relevant to only two groups of rate coefficients: those dealing with the release of reduced material from sediment once anaerobic conditions exist and those dealing with the oxidation of reduced materials dissolved in the water column upon reaeration.

PART II: MATERIALS AND METHODS

Sediment and Soil Sampling

7. Sediments from existing CE reservoirs were sampled for determination of anaerobic release rates. Sediment samples from the following reservoirs were used:

<u>CE Reservoir</u>	<u>CE District or Installation</u>
Eau Galle Reservoir, Wis.	St. Paul District
East Lynn Reservoir, W. Va.	Huntington District
Browns Lake, Miss.	Waterways Experiment Station (WES)
Beech Fork Reservoir, W. Va.	Huntington District
Eagle Lake, Miss.	Vicksburg District
DeGray Reservoir, Ark.	Vicksburg District
Lavon Lake, Tex.	Fort Worth District
Red Rock Reservoir, Iowa	Rock Island District
Greers Ferry Reservoir, Ark.	Little Rock District

8. Sediment samples from existing reservoirs were taken with a clamshell dredge or similar device. After sampling, sediments were placed in 208-ℓ steel drums with polyethylene liners, sealed with airtight lids, and transported to WES. Upon arrival at WES, sediments in each drum were stored at 20° C until sampling was conducted shortly thereafter.

Determination of Anaerobic Rate Coefficients

9. At WES, sediment samples from each reservoir were mechanically mixed, then placed in large-scale reactor units to a depth of 15 to 20 cm for experimental analysis. The general design of the 250-ℓ reactor units is shown in Figure 1. Construction and operation of the reactor units are discussed in detail in Gunnison et al. 1980. Reactor

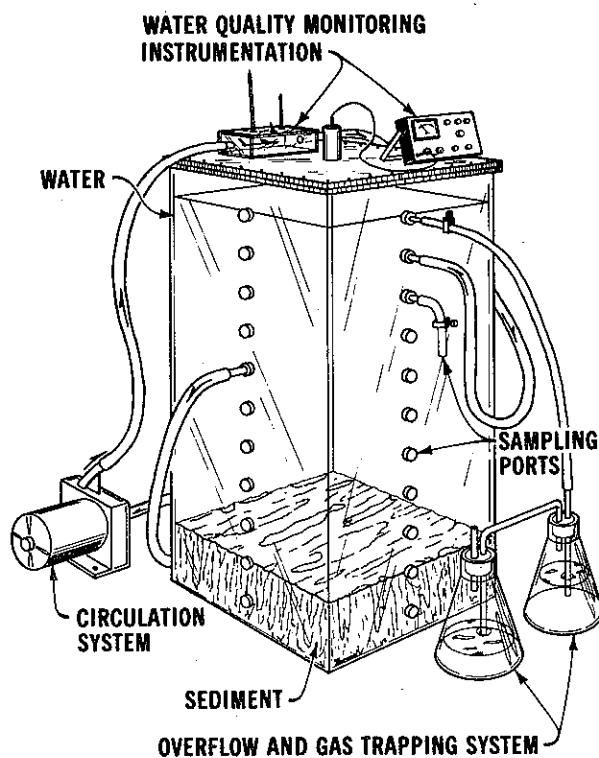


Figure 1. Design of large reactor units

chambers were maintained in an environmental chamber at a constant temperature (e.g., 20° C) throughout each experiment.

10. Prior to initiation of an experiment, 210 l of distilled water was added to each reactor unit, and the sediment-water contents of each unit were permitted to equilibrate for at least 30 days with constant aeration and mixing. After equilibration, an initial water sample was taken to provide baseline data under aerobic conditions. Then aeration was discontinued, and the reaction columns were sealed off from the atmosphere. The circulation pump that was used for mixing achieved a complete turnover of reaction column water once every 2 min; this ensured complete mixing of inflows with the water column, which allowed samples to be representative of the entire water column.

11. Reaction columns were run steadily for at least 100 days and sampled for various physical and chemical parameters (except dissolved oxygen (DO)) at 0, 10, 15, 25, 50, 75, and 100 days. The DO content was

measured daily from the initiation of the experiment to the point at which it was no longer detectable, or for a period of 30 days, whichever occurred first. In the latter case, DO was subsequently measured at 10-day intervals.

Determination of Aerobic Rate Coefficients

12. Mechanically mixed sediment samples were placed in either large-scale (250 l) (Figure 1) or small-scale reactor units (22 l) to a depth of approximately 15 cm for aeration studies. Construction and operation of different reaction chambers have been described in detail by Chen, Gunnison, and Brannon (1983) and by Gunnison and Brannon (1981). Aeration studies were conducted at a controlled temperature of 20° C, except where otherwise noted.

13. Prior to the initiation of aeration studies, reaction chambers were sealed for a 2- to 6-month period to develop anaerobic conditions as previously described. An initial water sample was then obtained to provide baseline information under anaerobic conditions. Then, aeration was initiated by purging with filtered laboratory air at a flow rate of 60 ml/min into the system through an airstone diffuser approximately 10 cm above the sediment-water interface. Dissolved oxygen concentrations were monitored and maintained at 7 ± 0.5 mg/l to simulate the estimated DO concentration of aerated anoxic bottom lake water (Chen, Keeney, and Sikora 1979). Aeration studies were continued for approximately 30 days, with periodic water sampling for determination of various physical and chemical parameters. Field experiments to obtain aerobic rate data have been described previously (Chen, Gunnison, and Brannon 1983).

Methods of Water Sample Collection, Preservation, and Analysis

14. Dissolved oxygen, pH, and conductivity were measured on samples collected by permitting water to flow gently from a reaction column sampling port into a standard biological oxygen demand (BOD) bottle.

Dissolved oxygen was determined with the azide modification of the Winkler method as described in Standard Methods (American Public Health Association (APHA) 1980) or estimated by using an oxygen meter (YSI Model 54, Yellow Springs Instruments, Yellow Springs, Ohio) equipped with an oxygen/temperature probe. Conductivity was measured with a YSI Model 31 Conductivity Bridge using a YSI Model 3403 Conductivity Cell. The pH was determined with a combination glass electrode. Temperature profiles, dissolved oxygen concentration, pH, and conductivity were measured during field studies with a HydrolabTM Transmitter Probe.

15. If a reaction chamber became anoxic, all procedures were conducted under a nitrogen atmosphere to maintain the anaerobic integrity of the samples; otherwise, tests were done under air. Samples to be analyzed for soluble nutrients or for dissolved total inorganic and organic carbon (TIC and TOC, respectively) were cleared of particulate matter by passage through a 0.45- μ membrane filter. Samples for dissolved metals analysis were passed through 0.10- μ membrane filters (Kennedy, Zellweger, and Jones 1974). Samples for total sulfide were taken and preserved simultaneously using zinc acetate; analysis was conducted immediately using the methylene blue method described in Standard Methods (APHA 1980).

16. Samples for total or soluble nutrients were preserved by acidification with concentrated HCl to pH 2 and immediate freezing and storage at -40° C. Samples for TOC and TIC analyses were processed immediately on a Beckman Model 915A Total Organic Carbon Analyzer equipped with an infrared detector.

17. Total Kjeldahl nitrogen and total phosphorus were converted to ammonium and inorganic phosphate, respectively, by digesting water samples on a semiautomatic digestion block (Ballinger 1979). Nutrient concentrations in water samples were determined using a Technicon Auto-analyzer II, in accordance with procedures recommended by the U. S. Environmental Protection Agency (EPA) (Ballinger 1979).

18. Sulfate concentrations were determined turbidimetrically following conversion of sulfate ion to a barium sulfate suspension (APHA 1980).

19. Metal samples were preserved by acidification with concentrated HCl. Metal concentrations were determined using direct flame aspiration with an atomic absorption spectrophotometer.

20. Parameters analyzed, analytical methods, detection limits, and units measured are presented in Table 1. For each parameter sampled, the methods of preservation and storage are identified.

Sediment Characterization

Total iron (Fe) and manganese (Mn)

21. A 2.0-g subsample of oven-dried sediment was weighed into a Teflon beaker containing 25 ml of 8 N HNO_3 . The mixture was digested for 1 hr at approximately 82° C on a hot plate (Carmody, Pearce, and Yasso 1973). The digest was then filtered through a Whatman No. 5 filter, brought to a final volume of 50 ml with distilled water, and stored prior to analysis.

Total Kjeldahl nitrogen (TKN) and total phosphorus (TP)

22. A subsample of water or sediment was weighed into a Technicon digestion tube containing the salt/acid/catalyst digestion mixture (Technicon Method No. 376-75 W/B). The mixture was digested for 4 hr at 380° C after the digest had cleared. The digest was allowed to cool, diluted with distilled water, and filtered, if necessary, through Whatman No. 5 filter paper. After cooling to room temperature, the digest was analyzed using methods 351.2 and 365.4 (Table 1) for TKN and TP concentrations, respectively.

Carbon

23. Total organic carbon was estimated after assessing total organic matter by weight loss following heating 10 g (oven-dry weight) of sediment for 5 hr in a muffle furnace at 550° C (Davies 1974). The resulting value was then multiplied by 58 percent to determine TOC (Allison 1965). Inorganic carbon content was determined by treating a 5.0-g soil subsample with 3 N HCl and then measuring the decrease in weight resulting from CO_2 loss (Allison, Bolles, and Moodie 1965).

Sediment Sampling Following Anaerobic Incubation

24. At the conclusion of anaerobic incubation, the sediment-water reactors were opened and the overlying water removed. Sediment cores, 7.5 cm in diameter, were then taken. Cores were immediately transferred to a glove box containing a nitrogen atmosphere. The sediment core was extruded from its liner into a flat plastic container in the glove box. The core was subsequently divided into sections 2.5 cm in thickness. Multiple cores were normally taken from each chamber, and similar depth segments were composited to obtain sufficient sample for analysis. A portion of each composited depth segment was placed into an oxygen-free, 250-ml polycarbonate centrifuge bottle in the glove box, followed by centrifugation at 9,000 rpm ($13,000 \times g$) for 5 min. Following centrifugation, the interstitial water was filtered under nitrogen through a 0.10- μ pore-size membrane filter and immediately acidified to a pH of 1 with concentrated HCl. The interstitial water was stored in polyethylene bottles and frozen until analyzed for NH_4^+ -N, orthophosphate-P, Fe, and Mn using methods previously described.

25. A subsample of each depth segment was placed into a pre-weighed container of known volume, weighed, then dried for 24 hr at 103° C. The sample was then reweighed, and sediment porosity (cm^3 of interstitial water/ cm^3 of sediment) was determined.

Quality Control

26. Analytical instruments were calibrated daily using certified standards traceable to National Bureau of Standards (NBS) reference materials. Sample blanks were processed for all analytical procedures, and NBS reference materials were analyzed as samples to check for possible procedural errors. The WES Analytical Laboratory Group participates in EPA round-robin quality control efforts. Statistical quality control efforts were incorporated daily as outlined in the EPA "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," (EPA-600/4-79-020, Environmental Monitoring and Support Laboratory,

Cincinnati, Ohio, pp 6-1 through 6-9). Every eighth sample was duplicated and spiked to ensure precision and accuracy. Quality control efforts also involved blind sample splits for precision evaluation and blind analysis of standard reference samples for accuracy evaluation.

Calculation of Rate Coefficients

27. Anaerobic rate coefficients were determined by performing linear regression analyses of mass release per unit area (mg/m^2) versus time. Anaerobic rate coefficients are in the form of fluxes ($\text{mg}/\text{m}^2/\text{day}$). Rate coefficients reported are the mean of three replicates.

28. Aerobic rate coefficients were calculated by performing linear regression analyses using the first order rate equation

$$\ln \left(\frac{C_t}{C_o} \right) = -Kt \quad (1)$$

where

C_t = concentration at time t (mg/ℓ)

C_o = initial concentration (mg/ℓ)

K = rate constant (day^{-1})

t = duration of oxidation (days)

The forms of the anaerobic and aerobic rate coefficients differ because of the importance of sediment in anaerobic reservoirs and the manner in which the CE-QUAL-R1 model handles anaerobic processes (Gunnison and Brannon 1981).

Statistical Analysis

29. One-to-one correlation analyses were performed using the Pearson product-moment correlation equation in the Statistical Analysis System (SAS) (Barr et al. 1976). To test for overall differences, analysis of variance procedures were utilized (Steel and Torrie 1960; Barr et al. 1976). Linear regression equations were determined using the least squares method.

PART III: RESULTS AND DISCUSSION

Anaerobic Rate Coefficients

30. Anaerobic rate coefficients obtained during the course of this study are presented in Table 2. These coefficients are in the form of fluxes of reduced materials from sediments ($\text{mg}/\text{m}^2/\text{day}$). A negative flux indicates that during the transition from aerobic to anaerobic conditions or during anaerobic conditions, the mass of that constituent in the overlying water decreased. A positive flux indicates that the constituent of interest was released to the water from the sediment. As can be seen, a wide variety of sediment-specific rate coefficients suitable for use in CE-QUAL-R1 and other water quality numerical models were obtained.

31. Anaerobic release rates presented in Table 2 for iron, manganese, and orthophosphate-P are lower than rates from the literature summarized in Gunnison and Brannon (1981). Release rates of total phosphorus and ammonium-N are in the same range as literature values (Gunnison and Brannon 1981). However, as pointed out in Gunnison and Brannon (1981), literature rates were generally obtained at lower temperatures than the 20°C used in this study. Fluxes of sulfide were measured in the DeGray and Red Rock studies. Sulfide, however, was rapidly precipitated by excess iron, as shown in Figure 2, and generally exhibited a sharp concentration increase followed by a rapid decrease. The concentration of sulfate was thereafter monitored as an indicator of overall sulfide production.

32. Once these rate coefficients have been calculated, the problem becomes the selection of the most appropriate coefficients for a particular reservoir. This process can be approached in a variety of ways, each of which should ensure that coefficients of the right order of magnitude are used.

Selection of Appropriate Anaerobic Rate Coefficients

33. Selection of appropriate anaerobic rate coefficients may be

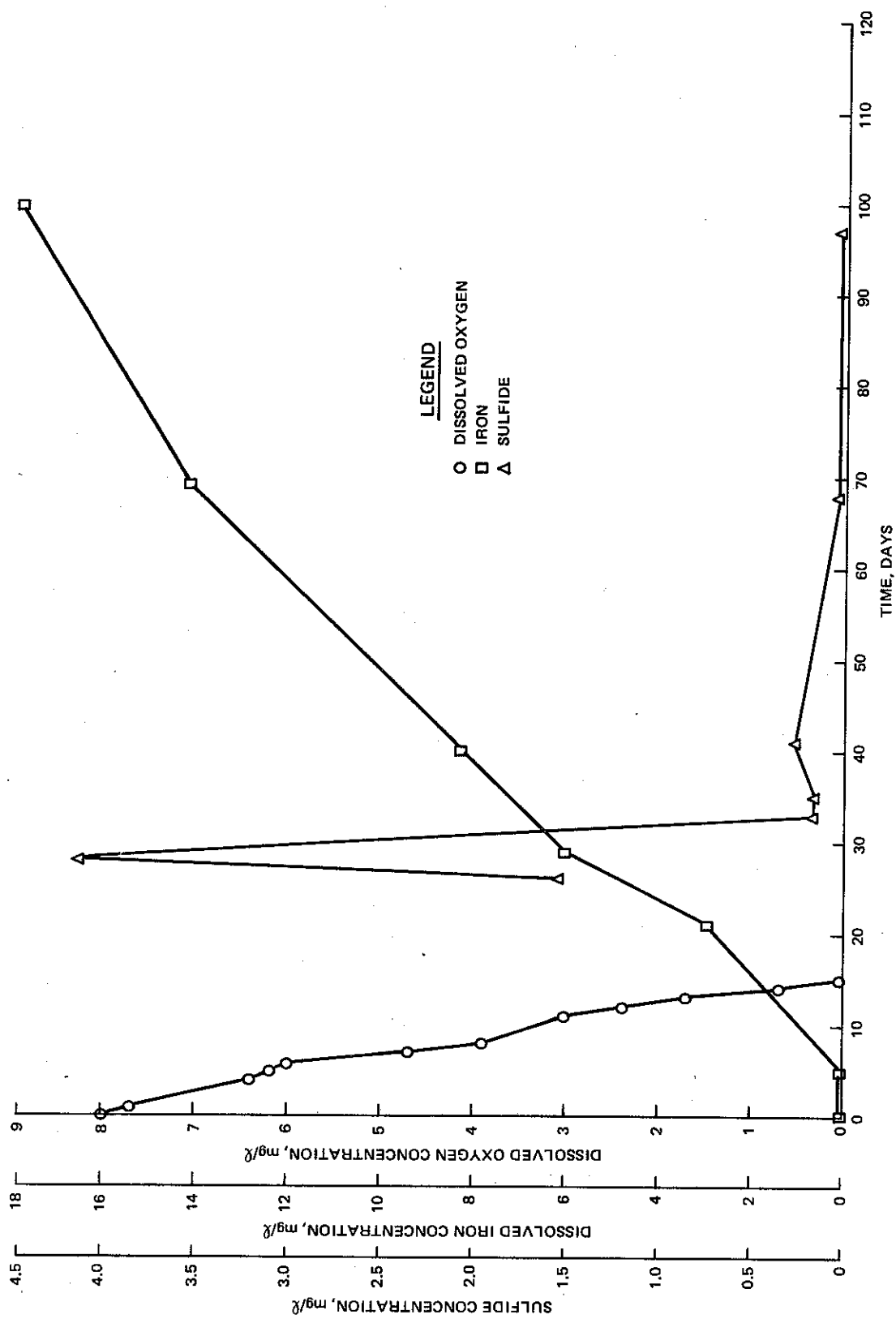


Figure 2. Changes in concentration of sulfide, iron, and dissolved oxygen in the water column of Red Rock reservoir sediment

approached in a number of ways, including (a) use of direct laboratory measurements or use of existing laboratory or field data from the reservoir concerned, (b) use of release rates from reservoirs near the project of interest, (c) use of release rates from reservoirs with similar chemical and physical properties to the project of interest, or (d) for some parameters, measurement of sediment interstitial water concentrations and sediment porosity.

34. Direct measurements using procedures in this report are one of the more accurate but difficult methods of determining release rate coefficients. Managers may also have at their disposal actual field measurements of parameters measured over time during anaerobic conditions. If such field data exist, information concerning the volume of anaerobic water, concentration changes over time, and the surface area of sediment exposed to anaerobic water will allow calculations of fluxes ($\text{mg}/\text{m}^2/\text{day}$) to be made.

35. If a reservoir is in the vicinity of a project for which rate coefficients exist, there is a strong possibility that rate coefficients will be similar. Prior to acting on such an assumption, managers should ensure that general water circulation and stratification in the reservoirs being compared are similar and that sediment accumulation and general sediment characteristics are also comparable.

36. Physical and chemical characteristics of sediments for which rate coefficients have been determined are presented in Table 3. Rate coefficients presented in Table 2 were not related to any of the sediment characteristics reported in Table 3. This was not surprising in view of the complexity of the physical and chemical processes influencing release of materials from sediments (Berner 1971; Klump and Martens 1981; Lerman 1979). However, if such data exist or can be obtained for an existing project of interest, similarities in content of organic matter and reducible substances such as iron and manganese should allow similar release rates to be used as a first approximation. Comparisons should be limited to existing projects since soil organic matter in pre-impoundment areas differs substantially from that of sediments in existing projects (Gunnison, Chen, and Brannon 1983).

37. In theory, fluxes of anaerobic constituents from sediment to overlying waters should be predictable. Flux of dissolved constituents across the sediment-water interface is driven by advective transport of the species in pore water solution and attached to sediment particles, as well as by molecular diffusion (Lerman 1979). However, in the reactor units in this study, there was no sedimentation, and fluxes of Fe, Mn, orthophosphate, and $\text{NH}_4\text{-N}$ were measured when the sediment column and overlying water were anaerobic. Therefore, in the absence of oxygen, there should be little chance for precipitation reactions to reduce the flux of these dissolved species. Under these conditions, advective transport and precipitation will be minimal and can be ignored, and the appropriate flux equation reduces to (Berner 1971):

$$J_s = -\phi_o D_s \left(\frac{\partial c}{\partial z} \right)_{pw} \quad (2)$$

where

J_s = flux ($\text{mg} \cdot \text{cm}_s^{-2} \cdot \text{sec}^{-1}$, where s denotes bulk wet sediment)

ϕ_o = porosity at the interface ($\text{cm}_{pw}^3 \cdot \text{cm}_s^{-3}$, where pw denotes pore water)

D_s = bulk sediment molecular diffusion coefficient ($\text{cm}_s^2 \cdot \text{sec}^{-1}$)

$\left(\frac{\partial c}{\partial z} \right)_{pw}$ = pore water concentration gradient at the sediment-water interface ($\text{mg} \cdot \text{cm}_{pw}^{-3} \cdot \text{cm}_s^{-1}$)

Porosities and interstitial water concentrations of Fe, Mn, $\text{NH}_4\text{-N}$, and orthophosphate-P measured in the various sediments are presented in Table 4. Bulk sediment diffusion coefficients were estimated using the value of the tracer diffusion coefficients (D_o) at 18°C of Li and Gregory (1974) and the relationship $D_s = D_o \phi_o^2$ to obtain an estimate of the bulk sediment diffusion coefficient (Lerman 1979). Values of D_o for Fe, $\text{NH}_4^+\text{-N}$, Mn, and orthophosphate-P used in calculating predicted fluxes were 5.82×10^{-6} , 16.8×10^{-6} , 5.75×10^{-6} , and $7.15 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$, respectively. Predicted fluxes calculated using Equation 2 must be

multiplied by the factor 8.64×10^8 to convert units to $\text{mg} \cdot \text{m}_s^{-2} \cdot \text{day}^{-1}$.

38. Fluxes of NH_4^+ -N, Fe, Mn, and orthophosphate-P computed using Equation 2 and appropriate sediment and interstitial water data are presented in Table 5. Comparison of these predicted fluxes with observed fluxes (Table 2) showed that observed fluxes, except for NH_4^+ -N, consistently exceeded those predicted by Equation 2. This indicates that processes at the sediment-water interface in addition to simple molecular diffusion were influencing releases, a phenomenon also noted by others (Eaton 1979; Klump 1980; Klump and Martens 1981). Calculating fluxes other than that of NH_4^+ -N would therefore result in underestimating releases, at times by an order of magnitude or more.

39. The most likely sediment interface effect was remobilization during anaerobic conditions of iron, manganese, and orthophosphate from compounds and complexes formed in the aerobic surface layer of sediments when the overlying water was aerobic (Eaton 1979; Duchart, Calvert, and Price 1973; Gorham and Swaine 1965), in addition to concentration gradient-supported diffusion. Addition of cellulose to the water column resulted in no significant change in pore water concentration gradients. Prior to being sealed, sediment-water reactors were allowed to incubate aerobically for at least 30 days. Coupled with the time required for the water columns to go anaerobic, sufficient opportunity was provided for an oxidized zone enriched in Fe, Mn, and orthophosphate to form.

40. Other studies (Klump and Martens 1981; Schippel, Hallberg, and Oden 1973) have found that phosphate release immediately following oxygen depletion in the overlying water exceeded flux predictions. In further support of this interface contribution to flux, the addition of cellulose to the reactor units, which settled on the sediment surface in our studies, resulted in significantly ($P < 0.05$) increased release of Fe and Mn and decreased release of NH_4^+ -N (Table 6) with no significant change in the pore water concentration gradient. Increased release of Fe and Mn was presumably due to increased microbial activity which, in turn, increased assimilation of NH_4^+ -N and possibly orthophosphate-P, and decreased their fluxes. Very little or no orthophosphate-P was

released from the two sediments without cellulose addition, complicating evaluation of cellulose impacts.

41. There does exist, however, an empirical relationship between predicted and observed fluxes of Fe and $\text{NH}_4^+\text{-N}$. These relationships are presented in Figures 3 and 4. Regression equations associated with each figure allow estimations of realistic Fe and $\text{NH}_4^+\text{-N}$ fluxes for use in CEQUAL-R1 and other water quality models. Similar empirical relationships could not be derived for Mn and orthophosphate-P. The average depth of the sediment concentration gradient was 8 cm for Fe and 11 cm for $\text{NH}_4^+\text{-N}$.

42. Due to the complexity of environmental factors affecting release of anaerobic constituents from sediments, there exists no single procedure for selecting anaerobic rate coefficients. Quantitative methods are presented herein for selecting Fe and $\text{NH}_4^+\text{-N}$ release rates. Selection of other rate coefficients can be approached on a site-specific basis using procedures presented in this section of the report.

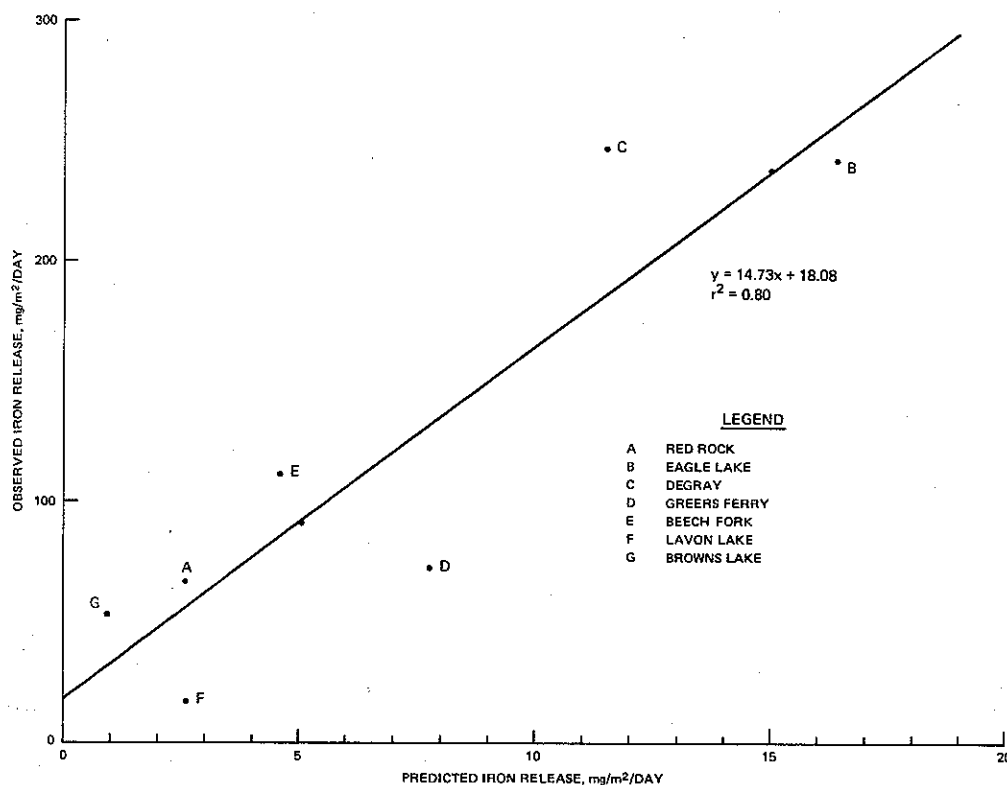


Figure 3. Relationship between predicted and observed releases of iron under anaerobic conditions

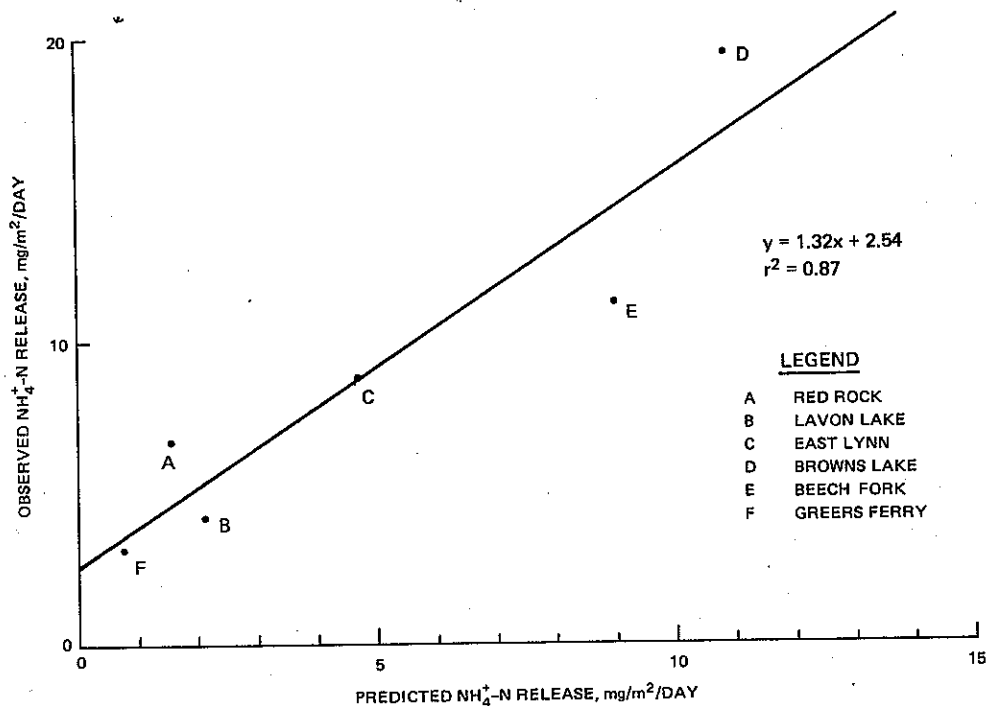


Figure 4. Relationship between predicted and observed releases of $\text{NH}_4^+\text{-N}$ under anaerobic conditions

Nutrient and Metal Accumulation Under Anaerobic Conditions

43. Release rate coefficients describe how rapidly a component is being added to or removed from the water column. The rate does not provide any information on the amount of reduced substances that will ultimately accumulate in the water column. The most important factors affecting the levels of reduced substances that accumulate in the water column are duration of stratification, duration of anaerobic conditions, rate of dissolved oxygen depletion, intensity of reduction, and concentration of the component of interest in the sediment.

44. The longer a reservoir remains stratified, the more time there is for oxygen to become depleted and for reduced substances to accumulate in the bottom waters, or in the metalimnion in projects subject to metalimnetic anoxia. If there is minimal oxygen demand, relatively long periods of stratification may not result in adverse water quality impacts. The major factor affecting the rate of oxygen depletion is the

amount of biologically available organic matter. As illustrated in Figure 5, the addition of cellulose as an external carbon source to DeGray and Red Rock sediment reactor units greatly increased the rate of dissolved oxygen depletion, resulting in complete depletion of dissolved

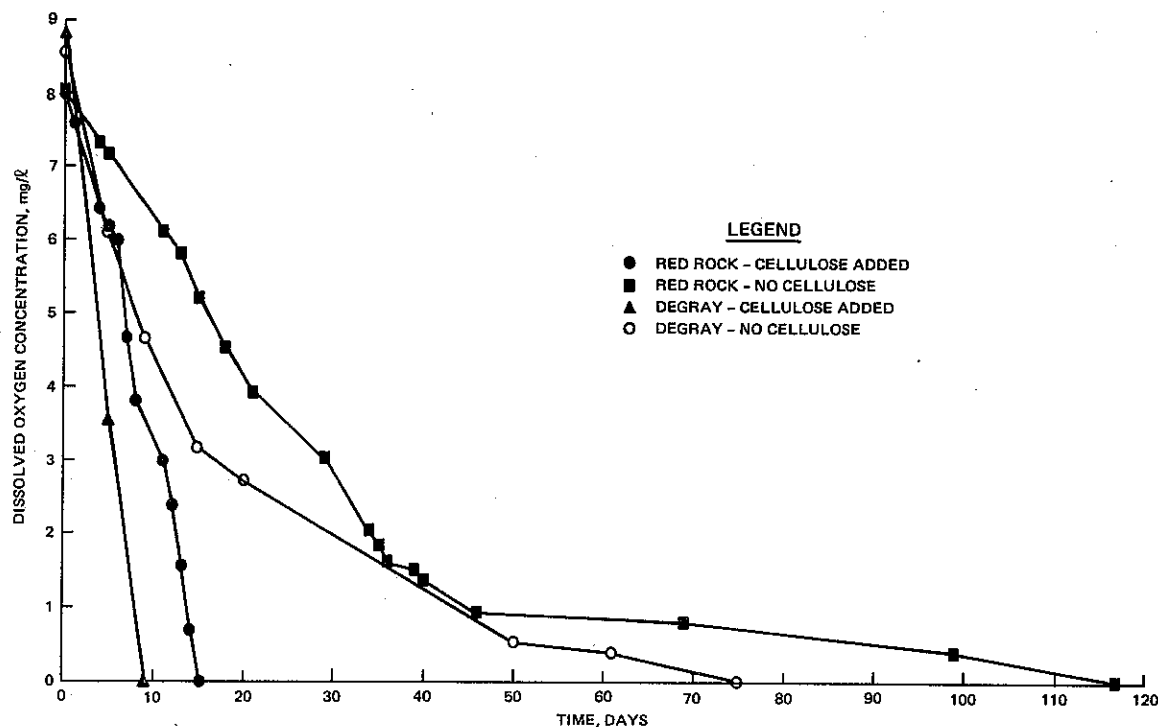


Figure 5. Effect of external carbon source (cellulose) on dissolved oxygen depletion

oxygen within 15 days. Much longer periods of time were required for depletion of dissolved oxygen when no external source of organic carbon was available. The rapid depletion of dissolved oxygen in cellulose-amended DeGray and Red Rock reactor units resulted in manganese release earlier in the stratification period. Release does not occur indefinitely, however, but generally reaches an asymptotic limit. An influx of organic matter may or may not result in a higher final concentration of manganese.

Aerobic Rate Coefficients

45. Aerobic rate coefficients obtained during the aeration studies

are summarized in Table 7. These coefficients are site specific and are expressed in units of day^{-1} . A negative K value indicates that during the transition from anaerobic to aerobic conditions, the oxidized constituent was produced in the overlying water. A positive K value indicates that during this period, the concentration of the constituent of interest decreased in the overlying water. A wide variety of sediment-specific rate coefficients suitable for use in CE-QUAL-R1 and other water quality numerical models were obtained.

46. It should be kept in mind that these rate coefficients, as well as the anaerobic rate coefficients, were obtained at 20°C . In the U. S., temperatures of reservoir hypolimnetic waters can range from 5°C to 25°C . In general, lower temperatures will slow the rate of transformation, while higher temperatures will accelerate it.

47. Following initiation of aeration, dissolved oxygen concentrations in anaerobic waters increased to an average of 4.4 mg/l during the first day and had reached 6.5 mg/l during the second day (Table 8). In most cases, the dissolved oxygen concentration of the overlying water attained a value of 7.0 mg/l following 2 weeks of aeration and remained at that level for the remainder of the incubation.

Field Validation

48. Various complex environmental factors can affect oxidation rates in CE reservoir systems. For this reason, field evaluations were conducted at Eau Galle reservoir, Wisconsin, during the summers of 1981 and 1982 to ascertain the degree of correspondence between aerobic rate coefficients derived from field and laboratory measurements. As shown in Table 9, there was good statistical agreement between field and laboratory rates for total inorganic nitrogen, $\text{NH}_4^{+}\text{-N}$, and iron oxidation. Statistical differences were noted between $\text{NO}_3^{-}\text{-N}$ accumulation, orthophosphate-P disappearance, and manganese oxidation rates in field studies compared to the values obtained in the laboratory. This disparity between field and laboratory results may have been due to dilution effects, water temperature variations, and other environmental factors

in the field. In a similar study, Chen, Keeney, and Konrad (1972) did not observe accumulation of NO_3^- -N and NO_2^- -N in lake water during destratification. Release of phosphorus from sediment under aerobic conditions was also reported by Holdren and Armstrong (1980).

Selection of Aerobic Rate Coefficients

49. The procedure for selecting appropriate aerobic rate coefficients is similar to that previously described for anaerobic rate coefficients, except that oxidation rates rather than release rates should be considered. Use of diffusional flux equations is also irrelevant for selection of aerobic rate coefficients.

50. A complete series of correlation analyses between aerobic rate coefficients, aerobic rate coefficients and sediment physical and chemical characteristics, and aerobic rate coefficients and water chemical properties were conducted to determine if any relationships for selecting aerobic rate coefficients existed. These analyses showed that some oxidation rate coefficients were related. Nitrate production rate was inversely correlated with ammonium-N disappearance rate ($r = -0.898$, $P < 0.04$), orthophosphate disappearance rate ($r = -0.938$, $P < 0.02$), and ferrous iron oxidation rate ($r = 0.931$, $P < 0.06$). Ferrous iron oxidation rate was also correlated with phosphate disappearance rate in the water column ($r = 0.787$, $P < 0.06$).

51. In some cases, sediment parameters were related to oxidation rates. Disappearance rate of total inorganic nitrogen was related to sediment TKN concentration ($r = 0.997$, $P < 0.01$) and sediment TIC content ($r = 0.828$, $P < 0.08$). Nitrate reduction rate was inversely correlated with sediment total carbon content ($r = 0.831$, $P < 0.08$). Oxidation rate of manganese was directly correlated with sediment iron ($r = 0.800$, $P < 0.06$) and sediment manganese ($r = 0.673$, $P < 0.14$). Use of sediment parameters in cases where significant relationships exist with oxidation rates will allow selection of an appropriate rate coefficient. Otherwise, aerobic rate coefficient selection must be based on existing laboratory or field data from reservoirs that are chemically

and physically similar or are geographically near the reservoir of interest. The complexity of the chemical and microbial processes that affect aerobic oxidation rates of reduced substances and the site-specific nature of such processes preclude more detailed aerobic rate coefficient selection guidelines.

Interpretation and Evaluation of Rate Constants

52. Rate data presented in this report were obtained at 20° C, a temperature closer to the norm for CE reservoirs than previously reported rate constants (Gunnison and Brannon 1981). However, if hypolimnetic waters of a project are substantially lower than 20° C (i.e., 10° C), then the rate reported herein may have to be reduced to adequately represent release rates at the lower temperature. Another study (Gunnison, Chen, and Brannon 1983) examined the effect of temperature on anaerobic release rates and oxygen depletion. It appeared that lowering temperatures approximately 10° C would result in halving of anaerobic release rates and oxygen depletion rates. This agreed well with the concept of Q_{10} , that for a 10° C rise in temperature, a doubling in reaction rates occurs (Hoar 1966). Halving reaction rates obtained at 20° C for reservoir waters at 10° C, if release rates would otherwise be similar, therefore appears to be a valid means of obtaining a rate coefficient estimate.

53. Interpretation and evaluation of the information obtained using these rate constants must be conducted within the context of CE-QUAL-R1. Incorporation of appropriate rate constants into anaerobic as well as aerobic subroutines of the model will allow evaluation of the impact of anaerobic conditions and reaeration on the reservoir ecosystem. This information will allow CE-QUAL-R1 users to predict water quality and evaluate control strategies for CE reservoirs.

54. Rate coefficients applicable to CE-QUAL-R1 and specific references to the CE-QUAL-R1 User's Manual (Environmental Laboratory 1982) are presented in Table 10.

PART IV: CONCLUSIONS

55. This report represents a compilation of anaerobic and aerobic rate coefficients suitable for use in the subroutines developed for CE-QUAL-R1. These coefficients cover a wide variety of reservoirs and are generally site specific in nature. Guidance is provided, however, to aid in selection of appropriate coefficients for reservoir systems that have not been studied.

56. Aerobic rate coefficients obtained in field and laboratory studies for total inorganic nitrogen, $\text{NH}_4^+\text{-N}$, and iron were not statistically different. In the field environment, $\text{NO}_3^-\text{-N}$ accumulation, orthophosphate-P disappearance, and manganese oxidation rates were not comparable to laboratory derived rates, presumably due to dilution and other complex environmental effects.

57. The rate data presented in this report are for use in CE-QUAL-R1 and other water quality models. Interpretation and evaluation of the information obtained using these rate constants must be conducted in the context of the overall ecological model.

REFERENCES

- Allison, L. E. 1965. "Organic Carbon," Methods of Soil Analysis; Part 2, Chemical and Microbiological Properties, C. A. Black, ed., American Society of Agronomy, pp 1367-1378.
- Allison, L. E., Bolles, W. B., and Moodie, C. C. 1965. "Total Carbon," Methods of Soil Analysis; Part 2, Chemical and Microbiological Properties, C. A. Black, ed., American Society of Agronomy, pp 1346-1366.
- American Public Health Association. 1980. Standard Methods for the Examination of Water and Wastewater, 15th ed., Washington, D. C.
- Ballinger, D. C. 1979. Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, EPA, Cincinnati, Ohio.
- Barr, A. J., et al. 1976. "A User's Guide to SAS 76," SAS Institute Inc., Raleigh, N. C.
- Berner, R. A. 1971. Principles of Chemical Sedimentology, McGraw-Hill, N. Y.
- Carmody, D. J., Pearce, J. B., and Yasso, W. E. 1973. "New York Bight," Marine Pollution Bulletin, No. 4, pp 132-135.
- Chen, R. L., Gunnison, D., and Brannon, J. M. 1983. "Characterization of Aerobic Chemical Processes in Reservoirs: Problem Description and Model Formulation" Technical Report in preparation, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.
- Chen, R. L., Keeney, D. R., and Konrad, J. G. 1972. "Nitrification in Sediments of Selected Wisconsin Lakes," Journal of Environmental Quality, Vol 1, pp 151-154.
- Chen, R. L., Keeney, D. R., and Sikora, L. J. 1979. "Effects of Hypolimnetic Aeration on Nitrogen Transformation in Simulated Lake Sediment-Water Systems," Journal of Environmental Quality, Vol 8, pp 429-433.
- Davies, B. E. 1974. "Loss-on-Ignition as an Estimate of Soil Organic Matter," Proceedings of the Soil Science Society of America, Vol 38, pp 150-151.
- Duchart, P., Calvert, S. E., and Price, N. B. 1973. "Distribution of Trace Metals in the Pore Waters of Shallow Water Marine Sediments," Limnology and Oceanography, Vol 18, pp 605-610.
- Eaton, A. 1979. "The Impact of Anoxia on Mn Fluxes in the Chesapeake Bay," Geochim. Cosmochim. Acta, Vol 43, pp 429-432.
- Environmental Laboratory. 1982. "CE-QUAL-R1: A Numerical One-Dimensional Model of Reservoir Water Quality; User's Manual," Instruction Report E-82-1 (Revised Edition; supersedes IR E-82-1, April 1982), U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

- Gorham, E., and Swaine, D. J. 1965. "The Influence of Oxidizing and Reducing Conditions upon the Distribution of Some Elements in Lake Sediments," Limnology and Oceanography, Vol 10, pp 268-279.
- Gunnison, D., et al. 1980. "A Reaction Chamber for Study of Interactions Between Sediments and Water Under Conditions of Static or Continuous Flow," Water Research, Vol 14, pp 1529-1532.
- Gunnison, D., and Brannon, J. M. 1981. "Characterization of Anaerobic Chemical Processes in Reservoirs: Problem Description and Conceptual Model Formulation," Technical Report E-81-6, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.
- Gunnison, D., Chen, R. L., and Brannon, J. M. 1983. "Relationship of Materials in Flooded Soils and Sediments to the Water Quality of Reservoirs; I, Oxygen Consumption Rates," Water Research (in press).
- Hoar, W. S. 1966. General and Comparative Physiology, Prentice-Hall, N. J.
- Holdren, G. C., Jr., and Armstrong, D. E. 1980. "Factors Affecting Phosphorus Release from Intact Lake Sediment Cores," Environmental Science and Technology, Vol 14, pp 79-87.
- Kennedy, V. C., Zellweger, G. W., and Jones, B. F. 1974. "Filter Pore Size Effects on the Analysis of Al, Fe, Mn, and Ti in Water," Water Resources Research, Vol 10, pp 785-791.
- Klump, J. V. 1980. Benthic Nutrient Regeneration and the Mechanisms of Chemical Sediment-Water Exchange in an Organic-Rich Coastal Marine Sediment, Ph. D. Thesis, University of North Carolina at Chapel Hill.
- Klump, J. V., and Martens, C. S. 1981. "Biogeochemical Cycling in an Organic Rich Coastal Marine Basin; II, Nutrient Sediment-Water Exchange Processes," Geochim. Cosmochim. Acta, Vol 45, pp 101-121.
- Lerman, A. 1979. Geochemical Processes, Wiley, N. Y.
- Li, Y. and Gregory, S. 1974. "Diffusion of Ions in Sea Water and in Deep Sea Sediments," Geochim. Cosmochim. Acta, Vol 38, pp 703-714.
- Schippel, F. A., Hallberg, R. O., and Oden, S. 1973. "Phosphate Exchange at the Sediment-Water Interface," Oikos (suppl.), Vol 15, pp 64-67.
- Steel, R. G. D., and Torrie, J. H. 1960. Principles and Procedures of Statistics, McGraw-Hill, N. Y.

Table 1
Analytical Methodology and Detection Limits
of Water Quality Parameters

<u>Parameter</u>	<u>Method</u>	<u>Detection Limit</u>	<u>Reference*</u>
Sulfate	375.4	5 mg/ℓ	MCAWW
Orthophosphate-P	365.1	0.01 mg/ℓ	↓
Nitrate-N	353.2	0.01 mg/ℓ	
Ammonium-N	350.1	0.01 mg/ℓ	
Total Kjeldahl nitrogen	351.2	0.10 mg/ℓ	
Total phosphorus	365.4	0.10 mg/ℓ	
Iron	236.1	0.05 mg/ℓ	
Manganese	243.1	0.05 mg/ℓ	
Sulfide**	427C	0.10 mg/ℓ	SMEWW
Dissolved oxygen	421B	0.02 mg/ℓ	SMEWW
Total inorganic carbon	505	1 mg/ℓ	SMEWW
Total organic carbon	505	1 mg/ℓ	SMEWW

* Methods of preservation and storage are given in the references, which are coded as follows:

MCAWW - U. S. Environmental Protection Agency. 1979. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268

SMEWW - American Public Health Association. 1981. Standard Methods for the Examination of Water and Wastewater, Washington, D. C.

** Detection limit for sulfide can be lowered several fold by use of zinc acetate to concentrate the sulfide (Method 427B, SMEWW).

Table 2

Anaerobic Rate Coefficients ($\text{mg}/\text{m}^2/\text{day}$) Derived from Reaction Chamber Studies

Parameter	Reservoir								Average Coefficient of Variation
	Lavon Lake	Beech Fork	Browns Lake	Eagle Lake	East Lynn	Eau Galle	Greers Ferry	DeGray Lake	
Iron	14.9	111.0	54.4	243.0	49.8	77.4	72.0	66.3	34.1
Manganese	4.5	148.0	91.3	33.1	13.8	45.0	36.1	39.1	9.7
Orthophosphate-P	2.3	NR	8.9	5.6	NR	NR	NR	2.6	NR
Ammonium-N	3.8	11.3	19.5	ND	7.3	NR	3.2	6.7	15.2
Total Kjeldahl N	NR	33.1	14.4	ND	11.1	NR	ND	46.9	20.0
Total phosphorus	NR	7.5	7.4	ND	NR	NR	ND	7.7	7.2
(Nitrate + Nitrite) - N	-1.57	-8.8	-6.2	ND	-7.1	-27.8	ND	-10.5	-2.3
Dissolved oxygen	-72.8	-226.3	-226.7	-137.5	-62.4	-236.0	-95.0	-125.0	-373.4
Soluble organic carbon	NR	NR	NR	NR	NR	NR	ND	NR	17.1
Sulfate	NR	-1064.0	-165.0	-170.5	NR	NR	ND	NR	NR
Sulfide	NR	ND	ND	ND	ND	ND	ND	289.0	17.0
									16.0

NOTE: NR = No release detected.
 ND = Not determined.

Table 3

Characteristics of Selected Sediments Used in the Laboratory Studies

Sediment	Particle Size Distribution			pH	Total				
	percent				Carbon percent	Kjeldahl Nitrogen percent	Total Phosphorus μg/g	Total Iron μg/g	Total Manganese μg/g
	Sand	Silt	Clay						
Beech Fork Reservoir	10.0	51.3	38.7	6.3	1.36	1.74	567.5	2,260	587
Browns Lake	13.8	57.5	28.7	7.0	2.77	2.22	748.1	19,467	794
Eagle Lake	17.5	27.5	55.0	7.3	1.94	2.12	782.9	20,142	644
Eau Galle Reservoir	70.0	16.3	13.7	8.1	3.87	1.81	480.2	6,585	462
Red Rock Reservoir	37.5	45.0	17.5	6.7	1.45	1.12	423.3	613	1182
Greers Ferry Reservoir	46.3	26.3	27.4	5.4	1.32	1.05	225.0	14,392	404
Lavon Lake	27.5	12.5	60.0	--	3.63	0.13	483.8	16,180	672
East Lynn Lake	0.0	52.5	47.5	5.4	1.74	0.71	37.8	6,167	283
DeGray Lake	9.0	61.0	30.0	7.0	2.05	1.60	80.9	2,365	401

Table 4
Porosities and Interstitial Water Concentrations
in Reservoir Sediments

<u>Sediment</u>	<u>Porosity</u> ϕ	<u>Concentration, mg/l</u>			
		<u>Fe</u>	<u>Mn</u>	<u>NH₄⁺-N</u>	<u>Orthophosphate-P</u>
Beech Fork	0.71	25.8	8.8	17.6	1.7
Browns Lake	0.73	3.4	7.2	15.2	1.2
East Lynn	0.68	71.9	6.0	13.0	0.3
Lavon Lake	0.82	9.5	3.0	2.7	ND
Red Rock	0.53	22.5	26.6	8.9	0.3
DeGray Lake	0.73	46.6	6.4	ND	ND
Eagle Lake	0.74	19.1	6.5	1.7	1.2
Eau Galle	0.55	21.9	8.5	ND	ND
Greers Ferry	0.64	55.7	18.9	2.0	1.1

NOTE: ND = Not determined.

Table 5
Fluxes (mg/m²/day) Calculated from Equation 2

<u>Reservoir</u>	<u>Parameter</u>			
	<u>NH₄⁺-N</u>	<u>Fe</u>	<u>Mn</u>	<u>Orthophosphate-P</u>
Red Rock	1.6	2.6	2.1	0.2
Lavon Lake	2.1	2.6	0.6	0.8
East Lynn	4.7	ND	1.1	0.1
Browns Lake	10.8	0.9	1.4	ND
Beech Fork	9.1	4.6	1.6	0.2
Greers Ferry	0.8	7.7	2.7	ND
Eagle Lake	ND	16.4	1.3	0.3
DeGray Lake	ND	11.5	1.2	ND

NOTE: ND = Not determined.

Table 6
Fluxes* of Sediment Constituents in Water to Which
30g Cellulose Has Been Added

Parameter	Red Rock		DeGray Lake	
	Cellulose	No Cellulose	Cellulose	No Cellulose
Fe	181.7 ± 12.1	66.3 ± 14.7	246.2 ± 45.3	34.1 ± 9.6
Mn	48.3 ± 1.6	39.1 ± 4.6	20.7 ± 1.7	9.7 ± 4.1
NH ₄ ⁺ -N	2.0 ± 1.4	6.7 ± 2.4	1.0 ± 0.1	15.2 ± 5.9
Orthophosphate-P	2.0 ± 0.9	2.6 ± 1.3	NR	NR

NOTE: NR = No release.

* Fluxes are presented as (mg/m²/day ±1 standard deviation).

Table 7
Aerobic Transformation Rates (K* day⁻¹) of Selected Nutrients
and Metals from CE Reservoirs at 20° C

Parameters	Reservoir					
	Beech Fork	Browns Lake	Eagle Lake	Eau Galle	Greers Ferry	Red Rock
Soluble organic carbon	0.106	0.073	0.052	0.091	-0.120	ND
Total inorganic nitrogen	0.007	0.071	0.034	0.120	0.015	ND
NH ₄ ⁺ -N	0.206	0.131	0.480	0.413	0.201	ND
NO ₃ ⁻ -N	-0.235	-0.251	-0.445	-0.538	-0.247	ND
Orthophosphate-P	0.150	-0.035	0.329	0.600	-0.037	0.235
Ferrous iron (Fe ⁺²)	0.281	0.461	0.840	1.881	0.444	0.111
Manganese (Mn ⁺²)	0.085	0.405	0.777	0.323	0.045	0.123
Sulfate	ND	-0.061	-0.111	-0.014	-0.120	-0.025

NOTE: ND = Not determined.

* K value was calculated using Equation 1.

Table 8
Changes in Dissolved Oxygen Concentration* in the
Overlying Waters During Aeration Studies

Time (day)	Reservoir						Average**
	Beech Fork	Browns Lake	Eagle Lake	Eau Galle	Greers Ferry	Red Rock	
0	0.0	0.2	0.0	0.0	0.0	0.0	0.0 ± 0.1
1	5.2	6.5	1.0	3.6	5.1	5.1	4.4 ± 1.9
2	6.9	7.0	4.6	6.3	7.2	7.2	6.5 ± 1.0
4	7.1	7.0	6.2	6.5	7.5	7.5	7.0 ± 0.5
7	7.6	6.9	6.3	6.4	7.5	7.5	7.0 ± 0.6
14	7.5	7.0	7.0	7.3	7.5	7.5	7.3 ± 0.2

* Measured in mg O₂/ℓ.

** Average value = mean ±1 standard deviation.

Table 9
Comparison of Chemical Oxidation Rate Coefficients*
Among Laboratory and Field Studies at
Eau Galle Reservoir, Wisconsin

Parameter	Field Study 1981	Field Study 1982	Laboratory Study	Significance Level**
Total carbon	ND	ND	0.091	--
Total inorganic nitrogen	ND	0.186	0.120	0.21
NH ₄ ⁺ -N	ND	0.192	0.413	0.64
NO ₃ ⁻ -N	ND	0.370	-0.538	0.00
Orthophosphate-P	ND	0.0	0.600	0.00
Iron (Fe ⁺²)	1.059	0.957	1.881	0.62
Manganese (Mn ⁺²)	0.856	0.537	0.323	0.01

NOTE: ND = Not determined.

* Unit: per day.

** Values >0.1 connote no statistical difference between means at 90 percent confidence level.

Table 10
CE-QUAL-R1 User's Manual References for Anaerobic
and Aerobic Rate Coefficients

<u>Parameters</u>	<u>Anaerobic Process (reduction) mg/m²/day</u>	<u>Aerobic Process (oxidation) per day</u>
Iron	TFEREL	TFE20X
Manganese	TMNREL	TMN20X
Orthophosphate-P	TXP4RE	--*
Ammonium-N	TCNREL	TNH3DK
NO ₃ ⁻ -N	--	TNO2DK
Soluble organic carbon	--	TDOMDK
Sulfate	TSO4RE	TSOXI
Sulfide	TSREL	TSOXI

* Not used in the CE-QUAL-R1 computer model.